

CIRCULATION COPY

SUBJECT TO RECALL
IN TWO WEEKS

UCRL- 92055
PREPRINT

CRYOPUMPING HYDROGEN ISOTOPE MIXTURES IN
MFTF-B WITH AND WITHOUT ARGON ADSORBENT

B. J. Schumacher
W. R. Call

This paper was prepared for submittal to the
Proceedings of the Sixth Topical Meeting on
the Technology of Fusion Energy,
San Francisco, CA, March 3-7, 1985.

February 12, 1985

Lawrence
Livermore
National
Laboratory

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government thereof, and shall not be used for advertising or product endorsement purposes.

CRYOPUMPING HYDROGEN ISOTOPE MIXTURES IN MFTF-B
WITH AND WITHOUT ARGON ADSORBENT

B. J. Schumacher and W. R. Call
Lawrence Livermore National Laboratory, University of California
P.O. Box 808, Livermore, CA 94550
(415) 422-1410

ABSTRACT

Mixtures of hydrogen isotopes, primarily deuterium (D_2), protium-deuterium (HD), and protium (H_2) must be pumped by the vacuum system in the Mirror Fusion Test Facility at Lawrence Livermore National Laboratory. In this study, we used argon as an adsorbent for cryopumping these isotopes at 4.2 K and found that deuterium will displace already adsorbed protium. Thus, when we pump mixtures of the two, sufficient argon must be supplied to adsorb both species. We also found that without argon, deuterium will cryotrap protium in accord with Raoult's law.

INTRODUCTION

The Mirror Fusion Test Facility (MFTF-B) under construction at Lawrence Livermore National Laboratory (LLNL) is a mirror fusion device designed to support experiments bridging the gap between smaller mirror machines and future fusion reactor designs. MFTF-B will operate on a 5-min. cycle consisting of a plasma shot in the first 30 s of each cycle followed by a 4.5-min. recovery. The vacuum requirements during this cycle are severe. The base pressure required for the 14×10^6 -liter vessel is less than 2.7×10^{-6} Pa with operating pressures during a plasma shot ranging from less than 8×10^{-6} Pa to less than 2×10^{-4} Pa depending upon the particular region of the vessel. The primary pumping is provided by more than 1000 m^2 of liquid-helium-cooled cryopanel at 4.5 K.

Our major concern when cryopumping at 4.5 K is the evacuation of helium and hydrogen isotope combinations of H_2 and HD (introduced as an impurity in the deuterium feed gas). An external vacuum system is provided on MFTF-B to pump the helium and H_2 . Previous MFTF-B

analyses in Ref. 1 assumed that the isotope combinations behave as independent species for cryopumping purposes. The result of this assumption was that HD would freeze on the 4.5 K cryopanel at an unacceptable base partial pressure of 2.7×10^{-5} Pa.

Argon was proposed as an adsorbent for HD in Ref. 1. This proposal called for argon injection underneath the liquid-nitrogen radiation shield because it was unclear whether the frost formed by argon injection through the liquid-nitrogen shield could provide the desired pumping effect. We needed to examine these injection methods and determine the effect of cryopumping mixed-hydrogen isotopes. References 2 and 3 indicate that, when helium is pumped onto argon, even small amounts of hydrogen destroy the sorbent capacity of argon-sorbent films. We were concerned that deuterium might have the same effect on the lighter hydrogen isotopes. Thus, to verify the adequacy of our MFTF design, we performed the following experiments to measure the pumping capacity of pre-deposited argon substrates at 4.2 K for mixed hydrogen isotopes.

EQUIPMENT AND PROCEDURE

We performed experiments using argon as an adsorbent for mixed hydrogen isotopes on an existing pumping assembly in the vacuum technology laboratory at LLNL. A schematic arrangement of the equipment is shown in Fig. 1. The system consisted of two chambers with an approximate volume of 130 liters for chamber (A) and 1300 liters for chamber (B). These chambers were connected by a 12-in.-diameter gate valve (V-1). The LHe cryopump was located in the smaller of the two chambers (A).

The pressure in both chambers was measured with nude Bayard-Alpert ionization gauges, which were located at room temperature. A tubulated residual gas analyzer (RGA) was mounted on chamber (A), but because of its mount arrangement was not suitable for measurement of partial pressures below 15×10^{-6} Pa.

*Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

MFM – Mass flow meter
LV – Leak valve
TM – Turbomolecular
IG – Ion gauge
LN – Liquid nitrogen
LHe – Liquid helium
V-1 – 12-in. gate valve
V-2 – 8-in. gate valve
RGA – Residual gas analyzer
A – LHe cryopumping chamber (130 liters vol)
B – Aux. chamber (1300 liters vol)

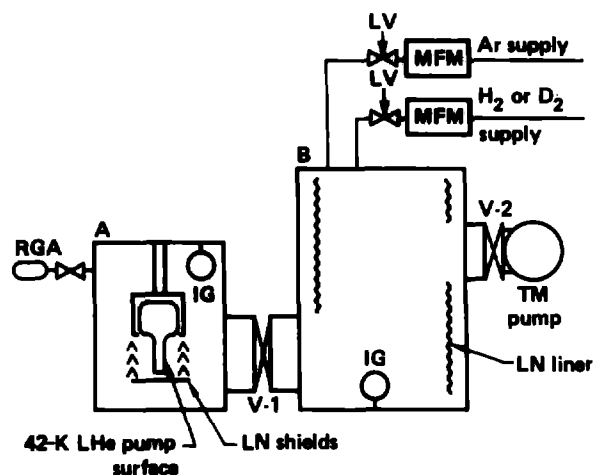


Fig. 1. Schematic arrangement of vacuum equipment used to perform the experiments.

The RGA was useful, however, for making qualitative interpretations during the course of a run. The ion gauges were checked for calibration by introducing pure protium into the chamber and reading the cryopump base pressure, which was 3.1×10^{-4} Pa [N₂ equiv]. The theoretical base pressure computed from Eq. (1) is 2.9×10^{-4} Pa [N₂ equiv].

$$P_B [\text{N}_2 \text{ equiv}] = \frac{P_{VP} \left(\frac{T_{\text{gauge}}}{T_{\text{vapor}}} \right)^{1/2}}{IG}, \quad (1)$$

where

$P_B [\text{N}_2 \text{ equiv}]$ = pump base pressure,

P_{VP} = equilibrium vapor pressure of protium⁴ at 4.2 K (8.4×10^{-5} Pa),

$(T_{\text{gauge}}/T_{\text{vapor}})$ = thermal-transpiration correction $(293/4.2)^{1/2}$,

IG = ion-gauge correction factor for hydrogen (2.4).

We considered this difference between the cryopump base pressure and theoretical base

pressure to be negligible and used the direct ion-gauge readings in our results.

We measured flows into the chambers with commercial mass-flow meters. The flow computed from the chamber rate of pressure rise ranged from 3% to 12% greater than those rates indicated by the mass-flow meters. We used the mass-flow meter values in our results.

Pumping speed and base pressures for adsorbing hydrogen on argon were measured as follows. We closed gate valve (V-1); and, before adding any gas, we recorded the background pressure in chamber (A). With valve (V-2) open to the turbomolecular pump, we established a stable flow of argon into chamber (B). An argon sorbent layer was deposited on the LHe cryopanel by closing valve (V-2) and opening valve (V-1), therefore, diverting the established flow to the cryopump. Then we closed valve (V-1) and rechecked the background pressure.

To investigate the adsorption of hydrogen isotopes or mixtures, we established each flow into chamber (B) in the same manner as above. Then we diverted the flow from the turbomolecular pump to the cryopump as above and recorded the pressure in chamber (A). We computed the pumping speed by dividing the flow by the recorded pressure. Periodically, we diverted the hydrogen flow back to the turbomolecular pump; and, after a stabilizing period of two minutes, we recorded the base pressure of chamber (A).

RESULTS

Figure 2 shows the chamber base pressure as a function of the argon-atom to hydrogen-molecule ratio in the frozen solid. Using the process described previously, we produced the curves in Fig. 2 by adding hydrogen to a pre-deposited argon substrate. The circled values at the left edge of the plot indicate the chamber background pressure prior to the introduction of either argon or hydrogen. The points plotted at the infinity argon-to-hydrogen ratio indicate the chamber background pressure after adding argon but before adding hydrogen. Adding argon had no significant effect on the chamber background pressure. Curve (a) resulted from pumping pure protium, curve (b) from pumping a mixture of 92% deuterium/8% protium, and curve (c) from pumping pure protium up to the point marked (*), then switching to pure deuterium. In general, the hydrogen contribution to the base pressure of the chamber did not become significant until the Ar:H₂ ratio had reached ~4:1 to 5:1. The base pressure of the chamber did not grow by more than 1×10^{-7} Pa [N₂ equiv] until the Ar:H₂ ratio of 5:1 was exceeded. Adjusting the 1×10^{-7} Pa [N₂ equiv] for thermal-transpiration and ion-gauge correction implies

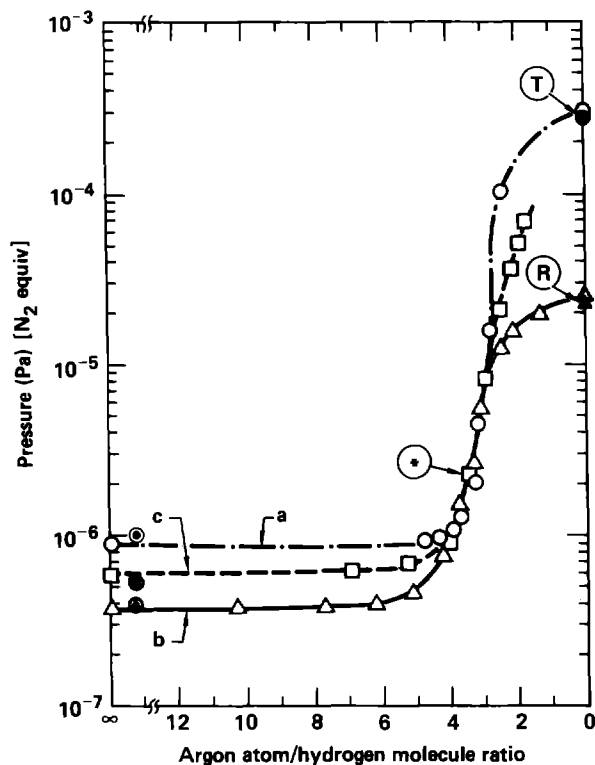


Fig. 2. Chamber base pressure when cryopumping hydrogen isotopes at 4.2 K on a predeposited argon substrate. The curves result from pumping:

- (a) Pure protium-- (T) is the base pressure computed from the protium vapor pressure.⁴
 - (b) 92%-deuterium/8%-protium mixture-- (R) is the base pressure computed from the pure component vapor pressures⁴ with Raoult's law.
 - (c) Pure protium up to the point marked (*), then switching to pure deuterium.
- The circled values near the left edge of the plot indicate the chamber background pressure (unknown composition) for each curve before the addition of either argon or hydrogen. The zero argon points were established during separate runs under cryocondensation conditions with no argon present in the chamber.

that the equilibrium hydrogen vapor pressure for Ar:H₂ ratio of 5:1 is on the order of 3×10^{-8} Pa.

The base pressure increases rapidly as the Ar:H₂ ratio is first driven below 5:1 by adding more hydrogen. The curves in Fig. 2 for pure protium (a) and the protium-deuterium mixture (c) appear to behave in an identical manner, implying that deuterium is able to displace protium from adsorption sites. To verify the above, we made one run, curve (b)

in Fig. 2, where we first loaded the argon with pure protium to an Ar:H₂ ratio of $\sim 3.4:1$ (marked with an (*)). We then switched from adding pure protium to adding pure deuterium and found that the base pressure continued to increase as if we were adding protium. This observation indicates that deuterium displaces previously adsorbed protium on a one for one basis.

The base pressure curves shown in Fig. 2 began to diverge after we added sufficient hydrogen to drive the Ar:H₂ ratio below $\sim 3:1$. The zero point (Ar:H₂ = 0) base pressures for the pure protium (a) and the 92%-deuterium/8%-protium mixture (b) were obtained by cryocondensing over 10^{18} molecules/cm² with no argon present in the chamber. Our findings show that the mixture used for curve (b) has a much lower base pressure than does pure protium. We observed that the base pressure of the mixture is stable for over 14 hours. We believe the lower base pressure of the mixture is the result of the protium being cryotrapped by the deuterium.⁵ We know from Refs. 4, 6, and 7 that the hydrogen isotopes form completely miscible solutions in the solid phase at 4.2 K and obey Raoult's law, which states: "The equilibrium vapor pressure above an ideal solution is equal to the sum of the pure component vapor pressures multiplied by their respective mole fractions in the solid phase." Thus, for the 92%-deuterium/8%-protium mixture, we compute the base pressure as follows:

$$P_{\text{mix}} = \frac{(X_H P_{\text{VP}} + X_D P_{\text{VD}}) \left(\frac{T_{\text{gauge}}}{T_{\text{vapor}}} \right)^{1/2}}{IG}, \quad (2)$$

where

- P_{mix} = [N₂ equiv] base pressure for the mix measured at 293 K,
- P_{VD} = equilibrium vapor pressure⁴ of deuterium at 4.2 K (5×10^{-9} Pa),
- X_H = mole fraction of protium (0.08),
- X_D = mole fraction of deuterium (0.92).

Thus, $P_{\text{mix}} = 2.3 \times 10^{-5}$ Pa. This zero-point base pressure for 92%-deuterium/8%-protium mix is plotted as point (R) in Fig. 2 for comparison. The point at which a given curve begins to diverge from the pack can be considered as the point at which cryocondensation begins to contribute to the pumping process.

The three base pressure curves in Fig. 2 were measured with an argon adsorbent layer of $\sim 1.3 \times 10^{18}$ atoms/cm², deposited at a rate of $\sim 3.6 \times 10^{15}$ atoms/cm²·s. Hydrogen was pumped on this substrate at a rate of $\sim 3.6 \times 10^{14}$ molecules/cm²·s. We varied these parameters

within the ranges listed below and did not observe any significant deviations from the curves in Fig. 2.

Argon thickness: 8.6×10^{17} to 3.8×10^{18} atoms/cm².
 Argon deposition: 1.3×10^{15} to 6.5×10^{15} atom/cm²·s.
 Hydrogen pumping: 1.9×10^{14} to 7.6×10^{14} atom/cm²·s.

Table 1 shows the pumping speeds we measured for the various gases including protium on an argon adsorbent. The sticking fraction for protium on a predeposited argon substrate appears to be very close to the sticking fraction for pure deuterium in cryocondensation because the ratio of their measured speeds is only slightly less than the theoretical speed ratio.

Table 1. Maximum pumping speed of the 4.2 K LHe test panel for the various gases pumped. Speeds listed are median values with the maximum data spread. Speeds for the protium and protium-deuterium mixtures decreased with increasing base pressure approximately as $(1 - P_B/P)^{1/2}$.^a

	Pumping speed (l/s)
Protium on Ar adsorbent	16,875 ± 950
92%-deuterium/8%-protium on Ar adsorbent	13,500 ± 300
92%-deuterium/8%-protium cryocondensing	13,800 ± 600
Deuterium	13,200 ± 400
Argon	4,300 ± 200

^a P_B = base pressure.

P = operating pressure.

CONCLUSIONS

Our experiments show that deuterium will cryotrap the lighter hydrogen isotope combinations as predicted by Raoult's law. The HD-base partial pressure in MFTF-B resulting from a 0.3% HD contamination in the deuterium feed gas will be less than 9×10^{-8} Pa. Protium will also be cryotrapped by the deuterium, but much less effectively because of protium's higher pure-component vapor pressure. We expect a protium outgassing rate of $\sim 3.4 \times 10^{-2}$ Pa l/s (Ref. 8) in MFTF-B that is

continuous while deuterium is added as a pulse with each shot. Thus the deuterium to protium ratio, which determines the base pressure for cryotrapping, depends on the shot frequency and fuel feed rates. A 100% duty cycle and fuel feed of ~ 500 Pa l/s, would be required to produce an average protium-base partial pressure of $\sim 1.3 \times 10^{-6}$ Pa, which still would exceed the requirements for MFTF-B. Thus the protium outgassing load must be pumped either by the external vacuum system or argon sorption.

Although the safety factor is small in the central-cell pressure because of conductive restriction at the axicell magnets, a separate analysis⁹ indicates that the external vacuum system is adequate to handle the expected MFTF-B protium gas load. Therefore, argon sorption will not be required for MFTF-B unless protium outgassing loads are greater than expected. If outgassing loads are higher than expected, additional protium pumping speed could be provided by injecting argon into the vacuum vessel rather than injecting argon under the liquid-nitrogen shielding. Because deuterium can displace protium from adsorption sites on the argon, sufficient argon must be supplied to adsorb all of the deuterium as well as the protium. To produce a base partial pressure for protium of less than 1.3×10^{-6} Pa will require a minimum of four argon atoms for each hydrogen molecule.

REFERENCES

1. L. E. Valby, Lawrence Livermore National Laboratory, Livermore, CA, unpublished notes (1984).
2. R. Dawbarn and J. D. Haygood, Development and Evaluation of a Cryodeposit Sorption Pump Capable of Pumping Helium, Arnold Engineering Development Center, Air Force Systems Command, Arnold Air Force Station, TN, AEDC-TR-68-90 (AD675207) (1968).
3. J. J. Thibault, J. M. Disdier, G. Arnaud, and J. C. Boissin, "Design and Preliminary Tests of the Liquid Helium Cooled MFTF Cryopumping System," J. Vac. Sci. Technol. 18(3), 1140 (1981).
4. P. C. Souers, Hydrogen Properties for Fusion Energy, Univ. of Calif. Press, Berkeley, CA, to be published 1985.
5. T. S. Chou and H. J. Halama, "Cryopumping of Deuterium Hydrogen and Helium Mixtures on Smooth 4.2 K Surfaces," Proc. 7th Inter. Vac. Congr. and Third Intern. Conf. Solid Surfaces, p. 65 (Vienna 1977), Brookhaven National Laboratory, Brookhaven, NY.

6. D. White and J. R. Gaines, "Liquid-Solid Phase Equilibria in the Hydrogen-Deuterium System," J. of Chem. Phys. 42(12), 4152 (1965).
7. N. G. Bereznyak, I. V. Bogoyavlenskii, L. V. Karnatsevich, and V. S. Logan, Melting Diagram of the pH_2 - oD_2 , pH_2 -HD, and oD -HD Systems, Sov. Phys.-JEPT 30(6), 1048 (1970).
8. D. D. Lang, Lawrence Livermore National Laboratory, personal communication (1984).
9. D. D. Lang and B. J. Schumacher, Lawrence Livermore National Laboratory, unpublished notes (1984).

BIBLIOGRAPHY

- J. Hengevoss, "Influence of the Temperature History of Condensed Argon on its Hydrogen Adsorptivity at Low Temperatures," J. Vac. Sci. and Technol. 6(1), 58 (1969).
- J. Hengevoss and E. A. Trendelenburg, "Continuous Cryotrapping of Hydrogen by Argon in the Temperature Range Between 4.2 and 15°K," Vacuum 17(9), 495 (1967).
- K. E. Templemeyer, "Sorption Pumping of Hydrogen by Cryodeposits - Sorption Capacity Measurement," Arnold Engineering Development Center, Air Force Systems Command, Arnold Air Force Station, TN, AEDC-TR-69-266 (AD700980) (1970).

